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16. ABSTRACT

This article is a summary of the literature published in the year 1985 on the topic of wastewater and water disinfection. It consists of a section on the microbiology and kinetics of disinfection and several sections related to the chemistry of disinfection, including analytical methods, reactions, and products.

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Disinfection

Albert D. Venosa, Russell Isaac

MICROBIOLOGY

Shevchenko and Taran[1] presented a survey on the feasibility of using chlorine in both water conditioning technology for evaluating the safety of potable water supply and in treating industrial wastewaters. Abu Dhabi City, the major center of population in the United Arab Emirates State of Abu Dhabi, has adhered to its 10-year policy of maximum reuse of treated wastewater effluent for municipal irrigation of roundabouts, gardens, and central reservations within the city.[2] Chlorination is used for disinfection, usually in the range of about 15 mg/L. Incomplete nitrification, which causes a build-up of nitrites, has had adverse effects on the chlorine disinfection process. Jones and White[3] reviewed the United Kingdom's policy of not disinfecting wastewater effluent and justified it by referring to communicable disease statistics; these have failed to show significant levels of waterborne disease communicated through surface waters. The reason for the review was the impending formation of a national committee to produce guidance concerning health aspects of the recreational use of natural inland waters. Burdarska[4] reviewed wastewater disinfection with ozone.

In pilot test comparisons of two types of in-line chlorine mixers, a jet and a conventional diffuser, Huang *et al.*[5] found that chlorine was reduced principally during the first 30 seconds of mixing, with higher reductions occurring with the jet mixer. The difference in mixing modes had no significant bearing on the coliform kills beyond the period of initial mixing, and significant coliform reduction continued to take place for up to 15 minutes after chlorine application, even though most of the kill occurred within the initial mixing period. Wang[6] achieved greater than 4.5-log reductions in bacterial counts within 200 seconds in wastewater effluent, using gaseous chlorine at a dose of 15–18 mg/L, as opposed to the dose of 25–32 mg/L within 7200 seconds using a chlorine solution method. Wang claimed a 94.5% reduction in initial construction cost because the gaseous chlorine method did not require the contact ponds necessary for the chlorine solution method. Gordon[7] verified findings from previous literature reports that facilities producing a highly nitrified effluent suffer an excessive chlorine demand because of the near absence of inorganic ammonium. Adding a small amount of ammonia substantially reduces this demand and still provides equivalent disinfection. Zeh[8] reported that bromine chloride provides an important ecological advantage when used in place of chlorine to disinfect wastewater effluent because its toxicity to fish is minimal. In addition, Zeh found it was more effective than either bromine or chlorine for cooling water treatment and is cost-competitive with other disinfectants that don't produce a residual.

Keswick *et al.*[9] found that Norwalk virus was more resistant to chlorine inactivation than poliovirus type 1, human rotavirus strain Wa, simian rotavirus strain SA-11, or f2 bacteriophage. A Norwalk virus inoculum exposed to 3.75 mg/L chlorine remained infectious for five of eight volunteers, despite the initial presence of free chlorine. It was hypothesized that this high chlorine explains the Norwalk agent's importance in outbreaks of waterborne disease. Grabow *et al.*[10] compared the chlorine resistance of hepatitus A virus (HAV) with other enteroviruses and bacterial indicators in wastewater effluent and broth enriched tap water. HAV survived longer than *Escherichia coli, Streptococcus fecalis,* poliovirus type 2, Coxsackievirus B5, and reovirus type 3, while it was less resistant than coliphage MS2, coliphage VI, simian rotavirus SA-11, and *Mycobacterium fortuitum.* They concluded that viruses and coliphages tend to be more resistant to combined

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chlorine residuals than bacteria, while in demand-free systems, the opposite is true. Young and Sharp[11] exposed monodispersed echovirus type 1 to chlorine and studied its inactivation kinetics in water. An initial 1- to 2-log decrease in titer was followed by a lag period, and this was followed by a final decline in titer. Inactivation kinetics with poliovirus type 1 was first order under the same conditions. The researchers suggested that the complex inactivation kinetics of echovirus is the result of shift in isoelectric conformational forms during exposure. Payment *et al.*[12] compared the resistance to chlorine of poliovirus and coxsackievirus isolated from environmental sources to resistance of laboratory strains of the viruses. Except for coxsackievirus CB5, isolates from environmental sources were not more resistant to chlorine than laboratory strains.

Under the experimental conditions of 21°C, pH 7.6 to 8.0, and 0.25 mg/L free chlorine, Kuchta *et al.*[13] found that *Legionella pneumophila* strains maintained in low-nutrient tap water were six to nine times more resistant than rich media-passaged isolates. Furthermore, samples from plumbing fixtures in a hospital yielded legionellae that were "super" chlorine resistant; after one agar passage their resistance declined to levels of comparable strains that had not been previously exposed to chlorine. LeChevallier *et al.*[14] studied the pathogenicity of waterborne bacterial pathogens after exposure to chlorine. They found that virulence determinants affected by chlorine differ from one pathogen to another. A decreased virulence of *Yersinia enterocolitica* after chlorine injury loss was not related to reduced attachment to Henle 407 intestinal epithelial cells but could be related to a loss of Hela cell invasiveness. In contrast, injured *Salmonella typhimurium* and enterotoxigenic *E. coli* cells lost their ability to attach to Henle cells. Hoff *et al.*[15] compared *in vitro* excystation and mouse infectivity as methods for quantitatively determining the viability of *Giardia muris* cysts before and after exposure to free residual chlorine. Results indicated an infectious dose comprised 1 to 15 cysts. *In vitro* excystation turned out to be an adequate indication of *G. muris* cyst infectivity for its host.

Selleck's empirical model for describing the kinetics of coliform decay in wastewater was shown by Haas and Karra[16] to be an adequate and justifiable predictor of inactivation behavior. Combining demand-free microbial inactivation rates with knowledge of the immediate chlorine demand of a given system and of the rate of conversion of free to combined chlorine makes it possible to estimate adequately the specific parameters necessary for designing a chlorination facility. Various antifouling treatment regimes using chlorine or slow-releasing bromine biocide were compared by Soracco *et al.*[17] for controlling the fouling of 304 stainless steel heat exchanger tubing. The authors found that low level continuous treatment was more effective than higher level intermittent treatment and that chlorine- and bromine-based compounds were similarly effective. Moss *et al.*[18] evaluated the concept of targeted chlorination to control biofouling in cooling water systems. The concept involves chlorinating a few condenser tubes at a time and mixing the small amount of discharged chlorinated water with the rest of the cooling water at the condenser outlet. Scotte[19] reviewed the manufacture and uses of chlorocyanuric compounds for wastewater and swimming pool disinfection, treatment of industrial water, and textile treatment, and use as cleaning agents and detergents.

Chlorine dioxide is used at treatment plants, pumping stations, and clean water reservoirs along the aqueducts of the River Maise in Brussels, Belgium. Masschelein[20] discussed the use of this chemical for bacterial disinfection and for preventing trihalomethane (THM) formation. Soprani *et al.*[21] reported on the use of chlorine dioxide as a disinfectant for wastewater effluents earmarked for crop irrigation and fertilization. Chen *et al.*[22] conducted an extensive evaluation of the kinetics of chlorine dioxide inactivation of *Naegleria gruberi* cysts in water. Inactivation was characterized by an initial concave downward shoulder followed by an essentially linear portion, but the process obeyed Watson's Law. An examination of concentration-time products for 99% cyst inactivation revealed that ozone has the lowest, followed by chlorine dioxide, and finally chlorine.

Gilpin *et al.*[23] studied continuous ultraviolet light (UV) and chlorine disinfection of circulating water systems for destroying *Legionella* and *Pseudomonas aeruginosa*. They concluded that UV disinfection of these systems may be an appropriate alternative or supplement to chemical biocides. Dutka[24] assessed the sensitivity to sunlight of *Legionella pneumophila* suspended in fresh and marine waters. The legionellae were more sensitive to sunlight in seawater than in fresh water. Comparisons with other bacteria revealed the following order of sensitivity to sunlight: natural lake water bacteria, *L. pneumophila*, *P. aeruginosa*, *E. coli*, and *S. fecalis*. Knudson[25] found that seven species of *Legionella* were very sensitive to low doses of UV light, but that all species effectively countered the germicidal effect when subsequently exposed to photoreactivating light. Borup and Adams[26] evaluated feasibility of removing suspended solids from wastewater lagoon effluents by UV irradiation followed by sedimentation. The process removed 30 to 54% of the solids from a typical lagoon effluent. Adequate disinfection was achieved as well. Qualls *et al.*[27] irradiated wastewater effluents in a system where the factors controlling disinfection could be accurately measured. They determined total coliform survival vs. UV dose for unfiltered and 10-μm filtered effluent samples. Particulate-associated coliforms were more resistant to UV disinfection than non-associated calls.

Severin and Suidan[28] discussed recent advances that have been made in the UV disinfection field such as rapid and complex inactivation kinetics, estimation of light intensity in UV reactors, light absorption and dispersion by wastewater constituents, physical and biological protection of microorganisms, effects of temperature, and effects of mixing on disinfection efficiency. Qualls and Johnson[29] developed and described a model that predicts bacterial survival in flow-through systems. The calculation takes into account the complex intensity patterns, non-ideal flow patterns, and non-linear curves of log survival vs. UV dose.

Kirkwold[30] reported that UV has been successfully disinfecting a full scale municipal treatment plant effluent since June 1983. At 47 300 m^3/d, it is the largest operating UV plant in the U. S. Operating costs were estimated to be $5.28/1 000 m^3, which were one-half to one-fourth the cost estimates for chlorination/dechlorination. The inactivation rate of poliovirus 1 by UV was measured by Yano *et al.*[31] in distilled water and treated wastewater. The latter required twice the dosage to effect 99.9% inactivation. Ansehrn[32] wrote a review of the use of UV as a water disinfectant in Europe. He reported that over 2 000 communities now disinfect their drinking water with UV, cost effectively. Chang *et al.*[33] measured the survival

of *E. coli, Salmonella typhi, Shigella sonnei, Streptococcus faecalis, Staphylococcus aureus, Bacillus subtilis* spores, poliovirus 1, simian rotavirus SA11, the cysts of *Acanthamoeba castellani,* and total coliform and total plate count organisms in secondary effluent. The doses for 99.9% inactivation of the vegetative bacteria, total coliforms, and standard plate count organisms were comparable. The viruses, spores, and cysts required 3, 9, and 15 times, respectively, the dose required for *E. coli.*

Chopin *et al.*[34] reported plasmid-mediated UV protection in group N *streptococci* for the first time. Griego *et al.*[35] studied the inactivation of nuclear polyhedrosis virus by various wavelengths of UV light (290, 300, 310, and 320 nm). All wavelengths inactivated the *Baculovirus,* but longer exposure times were needed at the higher wavelength.

The history and current status of the use of wastewater ozonation in the U. S. were reviewed by Robson and Rice,[36] who discussed problems manifested in first-generation facilities in the 1970s and improvements made in second-generation facilities in the 1980s. Smith *et al.*[37] compared the ozone disinfection efficiency of a complete mix reactor with a plug flow reactor on primary effluent. They reported that the plug flow unit achieved fecal coliform reductions equal to the complete mix unit but with less ozone. Anderson *et al.*[38] reported on a novel technique for achieving efficient ozone mass transfer to liquid, the spinning disc reactor. Rakness *et al.*[39,40] discussed the important factors affecting the dose needed to disinfect wastewater effluent with ozone. Contactor design, influent and target effluent coliform levels, and transferred ozone dose are the key influences. They presented a design approach that addressed these factors. In Vail, Colorado, an air-fed ozone disinfection process was reported[41] to have reliably achieved desired performance since start-up in October 1982. A deep, staged bubble diffuser contactor and adequately sized air drying equipment were key elements of the trouble-free operation. Reliable control of ozone disinfection was reported by Venosa *et al.*[42] to be possible using the product of off-gas concentration and liquid contact time by applying statistical reliability theory to determine the set-point. Automating the process in a closed-loop control scheme similar or analogous to that used in chlorination systems was reported in another paper[43] to effect significant annual operating cost savings over conventional methods of ozone dose control.

Richard[44] suggested that specific tests can be used to determine the design of ozone contactors, depending on the intended use of ozone (virucide, pollutant oxidant, clarification improvement, or wastewater disinfectant). Ahmad and Farooq[45] studied the influence of bubble size on ozone solubility and disinfection efficiency. They found that, for a given concentration of ozone at a constant gas flow rate, smaller bubble size resulted in an increase in ozone residual and the degree of inactivation of microorganisms, despite a decrease in transferred ozone dose to the wastewater. Ozone was effective in keeping the effluent from a night soil treatment plant in Japan free of coliforms.[46] The effluent was neither toxic to fish nor mutagenic. Stopka[47] reviewed experience with ozone in the treatment of cooling tower water. He found it to be a highly efficient sterilizer and excellent aid in microflocculation for organic slime removal. After 1 year of treatment, the turbidity of the ozonated cooling tower water was superior to that of chemically treated city water. Foller and Goodwin[48] reported further work on developing an electrochemical method of generating high concentrations of ozone and discussed oxidation kinetics involved in the use of electrochemically produced ozone in wastewater.

Ozone was found by Akey and Walton[49] to be a highly effective inactivating agent against Venezuelan Equine Encephalomyelitis Arbovirus. Complete liquid phase inactivation of the arbovirus was achieved with 0.025 mg/L ozone within 45 minutes of exposure. Harakeh and Butler[50] reported that the inactivation kinetics of ozone against viruses were exponential with respect to time and concentration. Human rotavirus was most resistant and coliphage f2 most sensitive. Neither temperature, added peptone, nor suspended solids significantly affected inactivation kinetics. Perrine *et al.*[51] studied the effect of ozone in inactivating various amoebic cysts in swimming pool water. Strains of *Acanthamoeba,* which were highly resistant to hypochlorous acid, were largely destroyed by ozonation, while *Naegleria,* a free-living amoeba, was equally resistant to ozone and chlorine.

Williams *et al.*[52] compared the bactericidal properties of the N-chloramine compound 3-chloro-4,4-dimethyl-2-oxazolidinone with calcium hypochlorite against *Staphylococcus aureus, Pseudomonas aeruginosa,* and *Shigella boydii.* In demand-free water, calcium hypochlorite was more effective, but in water containing organic matter, the N-chloramine compound was the better disinfectant. Petrov *et al.*[53] reported a synergistic bactericidal effect by combining chlorine and cobalt-60 gamma rays for inactivating 10^9 cells of *E. coli* in water and wastewater. Mucoid-grown staphylococci were found by Kolawole[54] to be substantially more resistant to disinfectants and antiseptics, because of the protective effect of the extracellular slime covering. Payment *et al.*[55] isolated poliovirus types 1, 2, and 3, coxsackie virus types B3, B4, and B5, echovirus type 7, and untyped picornaviruses from treated tap water. Sampling was conducted at all levels of treatment: raw water, postchlorination, postsedimentation, postfiltration, postozonation, and finished tap water. Cumulative virus reduction after filtration was 99.97% and did not significantly change after chlorination or ozonation. Removal efficiency of yeasts and acid-fast organisms by chemical coagulation and rapid sand filtration was found by Haas *et al.*[56] to be less than or equivalent to removal of total coliform organisms. LeChevallier *et al.*[57] examined microorganisms attached to granular activated carbon (GAC) for their susceptibility to chlorine disinfection. No decrease in viable counts occurred after 1-hr exposure to 1.5 mg/L free chlorine. The bacteria were found growing in cracks and crevices in the GAC particles and were coated with an extracellular slime layer. A substantial reduction in microbial count in the effluent of a wastewater treatment plant was observed by Van Dijck and van de Voorde[58] after 0.5% activated charcoal was added.

Chlorination of two papermill effluents neither improved nor degraded water quality in the receiving stream.[59] Disinfection was generally ineffective because of the large bacterial population and high chlorine demand of the effluent. A 5-year comprehensive water quality survey was made[60] of 10 public beaches and recreational sites in Washington, Oregon, and Idaho to gather baseline microbiological and physiochemical data for establishing recreational water quality criteria. The

authors concluded that, although the water quality met EPA guidelines for fecal coliforms, swimmers may still be at risk of illness related to enterococci. Karr *et al.*[61] used an index of biotic integrity to track changes in fish communities of streams subjected to various levels of chlorine and ammonia in association with treatment and discharge of wastewater. Results showed that chlorination in secondary wastewater treatment has a negative impact on the biotic integrity of the receiving streams studied. Furthermore, removal of ammonia in a tertiary treatment program did not improve biotic integrity in the receiving stream. Haas *et al.*[62] summarized studies on the presence of acid-fast and yeast organisms in water and wastewater treatment plants and in surface water. The authors concluded that these organisms satisfy most of the conditions as indicator organisms and are acceptable as indicators of disinfection efficiency. Hubly *et al.*[63] published a risk assessment report of wastewater disinfection. They presented a data base for chlorination with and without dechlorination, ozonation, and ultraviolet radiation. Energy consumption and cost analyses were also presented for chlorination and ozonation, along with example risk calculations for two hypothetical treatment plants.

ANALYTICAL PROCEDURES

Kaab and Huber[64] described a variation of the standard amperometric back titration which adds iodine titrant *in situ* electrochemically rather than as a solution, and monitors all phases of data collection, including detecting the end point, through a computerized system. The new instrumentation allows for the routine determination of parts per billion (ppb) total residual chlorine (TRC) in wastewater samples with estimated standard deviations of 14 ppb or less. Davies and Huber[65] described a voltametric method for determining monochloramine (NH_2Cl) in water; the potential selected minimized responses from HOCl and NH_3. Responses beyond the breakpoint were also minimal. Two organic chloramines failed to yield any signal under these conditions, so the technique may be selective for NH_2Cl. Jaworske and Helz[66,67] described a rotating ring disc electrode system used to monitor the rapid oxidant demand in natural waters. Results from estuarine water samples were used to estimate a second order rate constant of 10^7 L/mol·s for the rapid demand reaction. Finger *et al.*[68] described a system that measures and controls chlorine at a zero concentration using conventional chlorine residual analyzers and flow proportioning equipment.

Nutt *et al.*[69] conducted bench scale tests on four automatic total residual analyzers. These investigators revealed significant differences in the performances of the systems examined.

Dreux *et al.*[70] used high-performance liquid chromatography with two separate substrates, Zorbox C18 and Zorbox C8. The detectable limits noted in these ion pair chromatography experiments were inadequate for a direct determination of the chlorinated inorganic anions common in drinking water. Detection sensitivity may be improved by various means, including superior detectors. Gibbs *et al.*[71] found good reproducibility in using XAD resins to remove organic constituents from environmental samples.

Saksa and Smart[72] discussed the measurement of chlorine dioxide (ClO_2) using a chemiluminescent method combined with a membrane flow cell. The response was linear from 0.050 to 1.5 ppm of ClO_2.

STABILITY OF DISINFECTANTS

Morris[73] reviewed the reaction dynamics of chlorine in water with the emphasis on trichloromethane formation from fulvate and the breakpoint reaction with ammonia.

LeCloirec and Martin[74] studied the effect of chlorinating some naturally occurring amino acids. Experiments with alanine, phenylalanine, and tyrosine revealed a breakpoint pattern for the first two when chlorine concentrations were varied, but not with tyrosine. Both aldehyde and nitrite formation were detected in chlorinated solutions of α-alanine at pH values between 5 and 9. Ayotte and Gray[75] demonstrated that peptide nitrogen can take up chlorine in acidic solutions. Acetylglycine was the model nitrogenous compound employed.

Valentine[76] studied the disappearance of monochloramine in the presence of nitrite. The process is complex and the rate of NH_2Cl disappearance in the presence of NO_2^- greatly exceeded the rate based on a simple NH_2Cl hydrolysis. There also seems to be a dependence on the concentration of $[H^+]$ and an increased dependence on excess NH_3. Haag[77] examined the reaction of dimethylchloramine with Br^-. The reaction produced $(CH_3)_2NBr$ and was found to be first order in the concentrations of $(CH_3)_2NCl$, Br^-, H^+ and free HOBr. Also, the rate increased with ionic strength.

The decomposition of several chemicals used for disinfection were evaluated. Christina *et al.*[78] examined the decomposition of bromamine in aqueous solution. Where NH_2Br and $NHBr_2$ predominate, the reactions follow second-order equal kinetics. Where NBr_3 predominates, the reaction follows first-order kinetics. When NBr_3 and $NHBr_2$ are both present in significant concentration, the reaction is complex, presumably a mixture of both pathways. Dotson and Helz[79] studied the disappearance of residual chlorine in nonphotolyzed water dosed with 10 mg/L of chlorine. Once the breakpoint reaction was satisfied, the decay curves were similar. Humic acid in distilled water yielded a good model for the behavior observed in natural waters. Zika *et al.*[80] conducted experiments on the sunlight-induced decomposition of chlorine dioxide. The authors reported both ClO_2 and ClO_2^- are readily decomposed by sunlight and fluorescent lights.

Qualls and Johnson[81] described a generic model for chlorination of natural waters. The reactants considered, besides chlorine, were ammonia chloramine-forming organic nitrogen represented by glycylglycine, and fulvic substances. Isaac *et al.*[82] formulated a model of the reactions of bromide with ammonia and organic nitrogen compounds at concentration ratios less than the breakpoint. Valentine and Jafvert[83] and Inman and Johnson[84] discussed the mechanism for dibromamine formation.

Isaac and Morris[85] reported possible mechanisms for the direct transfer of active chlorine from chloramine (NH_2Cl) to organic nitrogenous compounds. In addition to direct transfer, hydrolysis of NH_2Cl can be a significant pathway at low concentrations (10^{-5} mole/L) of chloramine and organic amine nitrogen.

FORMATION AND CONTROL OF BYPRODUCTS

Seeger *et al.*[86] determined that the products from humic acids and chlorine at low concentrations were similar to those found in earlier studies that use much higher concentrations

of chlorine. Scully *et al.*[87] determined the yield of trihalomethane (THMs) from four proteins. While the yields were low, less than 0.51%, high concentration of proteins could be a significant source of THMs. de Leer *et al.*[88] found that the chlorination of humic acids produce several compounds that can be regarded as precursors for chloroform. In particular, the evidence pointed strongly to 1,3-dihydroxybenzene structures as having an important role. It has yet to be demonstrated, however, that these structures form an important part of the humic acid frame.

Amy *et al.*[89] and Gould *et al.*[90] examined factors influencing the incorporation of bromide and iodide into THMs. Bromine is incorporated into THMs to a much greater degree than iodine, especially at the iodide concentrations in normal environments.

Jensen *et al.*[91] studied the reaction of NH_2Cl with fulvic acid. They found no products that are ether-extractable from an acidified solution and detectable by GC/FID techniques. Total organic halide studies show monochloramine produces TOX that are more hydrophilic and larger than chlorine-produced TOX. Arber *et al.*[92] reported on attempts to minimize THM production during the disinfection of drinking water at Thornton, Colo. Both off-stream and on-stream chloramination were tried. The off-stream system produced the least amount of THMs but caused concern about varying bacterial quality. Kearney and Sansone[93] examined the formation of mixed N-halogenated methylamines by chlorinating in solutions of artifical sea water. Formation of CH_3NHCl, CH_3NCl_2, CH_3NClBr and CH_3NBr_2 was detected over the range of conditions examined.

Norwood *et al.*[94] found that trichloroacetic acid (TCAA) is an important and possibly ubiquitous by-product of drinking water disinfection with chlorine. These investigations used an isotope dilution gas chromotography/mass spectrometry method to determine TCAA at the microgram per liter concentration.

Duguet *et al.*[95] studied the conditions under which chloropicrin forms. The impetus for these studies was the detection of this toxic compound in two drinking waters that are prechlorinated. The researchers found that precursors may include a variety of organic nitrogen compounds, as well as organic compounds analogous to the THM precursors. Chloropicrin can be removed by granular activated carbon or by the abandonment of prechlorination. Brucket *et al.*[96] characterized chlorinated hydrocarbons formed through the chlorination of two potable water supplies. In one supply, the identified compounds accounted for approximately 45% of the TOX. The main fraction of TOX in surface or chlorinated waters corresponded to low-molecular weight organic compounds (<1000). Reckhow and Singer[97] explored some of the mechanisms in the formation of chloroform, trichloroacetic acid and dichloroacetic acid from the chlorination of humic materials. The model developed from these findings was then used to explain the effects of preozonation on organic halide formation potential of an aquatic fulvic acid. Rice,[98] in his review of recent uses of ozone for potable water treatment in the U. S., listed nine of 28 facilities as evaluating or using ozone for control of THM precursors. Kruithof *et al.*[99] related their findings on the effect of various unit processes in reducing THM formation. Granular activated carbon was effective only for short run times while ozonation was more effective. By far the best results were accomplished by GAC filtration followed by ozonation before chlorination. Veenstra and Khan[100] found that direct filtration of source water did not reduce THM formation to the degree needed. Feldstein *et al.*[101] found about a 30% reduction in THM production from river water when cyanuric acid exceeded HOCl by a molar ratio of at least 1.1 to 1 than when HOCl (13 mg/L) alone was used. Whether this difference would persist at chlorine concentrations representative of those used in drinking water and a health assessment of cyanuric acid remains to be established.

Kringstad *et al.*[102] reported the formation of chlorinated phenols when chlorlignins formed during the bleaching of softwood kraft wood pulp were subjected to further chlorination similar to that expected in water disinfection. Becher *et al.*[103] used high-performance size exclusion chromotography to identify products formed by the chlorination of humic materials. The results revealed bound organic chlorine in all molecular weight fractions and the degradation of high molecular weights. Uhler and Means[104] reported the formation of THMs on the chlorination of surfacial sediments from the Potomac River. Brominated THMs dominated when the sediments were taken from the more saline portions of the estuary. de Leer *et al.*[105] chlorinated terrestial humic acid solutions at a chlorine-to-carbon ratio commonly used in the production of drinking water. The reactions produced several compounds that can be regarded as precursors for chloroform and C-4 diacids. Whether these precursors form the only source of chloroform cannot be concluded, but they strongly point to the important role of 1,3 dihydroxybenzene structures as the primary source. The magnitude of their occurrence in humic acids has not been established.

Helz *et al.*[106] reported a decrease in THM formation through dechlorination. Reduction of $CHCl_3$ seemed to exceed that of $CHBrCl_2$ in the cooling water studied. Edzwald *et al.*[107] found that UV absorbance at 254 nm is a good surrogate parameter for trihalomethane formation potential. Cooper *et al.*[108] reviewed 107 references from the period 1946 to 1984 concerning the formation of THMs from bromine chloride, chlorine dioxide-bromide, and monochloramine-bromide solutions. Only the first combination produces THMs; some slight amounts are produced from ClO_2 mixtures but this is probably attributable to trace amounts of HOCl. Howard *et al.*[109] found that under acidic conditions, resorcinol diacetate and resorcinol dimethyl ether produced minimal concentration of THMs when chlorinated in seawater.

Welch *et al.*[110] reported on the use of polymaleic acid as a model organohalogen precursor. Cooper and Koganowicz[111] reported on a novel precursor of trihalomethanes, α-methylbengalamine.

OTHER CHEMISTRY

Haag and Hoigne[112] found that singlet oxygen can be effective in oxidizing selected organic compounds, but would be effective in material or wastewater treatment only when organic dyes are added to increase the concentrations of the oxidant. Cherry and Jessen[113] evaluated the use of polymer-bound dyes to oxidize chlorophenols without having to add dyes to the solutions. Their results demonstrated the effectiveness of the oxidation, but evaluation of the general application of this process requires experiments with actual waters or wastewaters. Nowell and Crosby[114] studied the interaction of

chlorinated solutions of selected aromatic compounds with light. They found that at least for aromatic compounds, free-radical oxidants formed from the photodegradation of HOCl/OCl^- seem to hydroxylate even deactivated rings, generating phenols that will react thermally with residual chlorine.

Sorrell *et al.*[115] assessed the use of purgeable and total organic halide (POX and TOX, respectively) as surrogates for determining individual volatile organic chemicals (VOCs), particularly in groundwater. They concluded that POX seems to be a more reliable technique for screening uncharacterized groundwaters for halo-VOCs at low concentrations. Stevens *et al.*[116] reported on the uses of total organic halide (TOX) as an indication of water quality. Measurements of OX in wastewater primarily identify compounds of industrial origin, whereas, in drinking water, the presence of disinfection by-products is indicated. The TOX measurement can be used as a simple means to verify the absence of OX combination without the need to conduct more sophisticated and expensive tests for various categories of TOX compounds.

Worley *et al.*[117] reported on further studies of the organic N-chloramine, 3-chloro-4, 4-dimethyl-2-oxazolidinone (agent I) and its bromine analog (agent IB). Agent I was an effective disinfectant but not as rapid acting as $Ca(OCl)_2$. THM production was confined to some chloroform but at concentrations about an order of magnitude lower than those produced by using $Ca(OCl)_2$. Agent IB seems to have considerable potential as an all purpose disinfectant.

Fiquet[118] compared chlorination and bromination of seawater with varying amounts of ammonia. At Cl:N ratios greater than 2, bromine produced by reaction of chlorine with bromide reacts with ammonia in a manner similar to that when seawater is brominated. At Cl:N ratios less than 2, both chloramines and bromamines are formed. The persistence of the residual chlorine is less than that of monochloramine. Sansone and Kearney[119] measured the kinetics of the loss of free and combined chlorine-produced oxidants (CPOs) and the production of halocarbons in surface and deep tropical seawater. The reactions were about a hundred times slower than those previously reported for temperate and semitropical coastal seawater. The precise explanation for this phenomenon is not clear. Significant concentrations of ClO_3^-, BrO_3^-, and bromoform can be produced. Haas and Brncick[120] examined the influence of sodium, potassium, and lithium on hypochlorite solution equilibria. They determined that measurable association exists between these cations and the hypochlorite anion. These neutral ion pairs may explain a report that free chlorine was a more effective disinfectant for viruses at high pH than at low pH, in contradiction to other reports.

Voudrias *et al.*[121] studied the effects of activated carbon on the reactions of free chlorine with phenols. They reported that phenols adsorbed on granular activated carbon reacted with chlorine to hydrolyze the aromatic ring, oxidize the phenols to quinones, as well as to result in chlorine substitutions, carboxylation and oxidative coupling (dimer formation). Chlorohydroxybiphenyls (hydroxylated PCBs that are *in vivo* metabolites of PCBs) also were formed. Robinson *et al.*[122] evaluated the impact of novel tentacle molecules on the chlorination of phenol in aqueous and methanolic solutions. Vakulenko *et al.*[123] reported on the reaction of nitrophenols and chlorine in dilute aqueous solutions.

Mayadeo and Pandit[124] reported that the reduction in BOD per mg/L chlorine consumed depends on the stage and state of wastewater at which the chlorine is applied. Axegaard[125] reported that the formation of organically bound chlorine decreased almost linearly with increasing ClO_2 substitution in the bleaching of softwood kraft pulps. Bergnor *et al.*[126] reported that the chlorate formed during ClO_2 bleaching of pulp can be greatly reduced by treating the waste liquors with SO_2. Concern about the chlorate concentrations centered on its potential toxicity to seaweed.

Gurol and Breman,[127] and Gurol *et al.*[128] reported on the kinetics and mechanism of ozonation of free cyanide species in water using stopped-flow spectrophotometer. The rate constant was estimated to be 2600 $(mole/L)^{-1}\ s^{-1}$. Experiments indicated stoichiometric conversion of cyanide to cyanate.

Montiel and Ouvrard[129] reported on pilot plant studies of cyanide removals through the use of several treatment processes, including ozonation. Biological treatment to remove the cyanide was considered more effective in this case. Narkis *et al.*[130] studied ozonation of non-ionic surfactants in aqueous solutions. Sharma and Pachauri[131] studied the reaction of ClO_2 with dl-alanine. Aieta *et al.*[132] reviewed the chemistry of oxo-chlorine compounds relevant to ClO_2 generation.

Watt *et al.*[133] discussed the characteristics of activated sludge effluents before and after ozonation. Among their findings were the facts that organic matter with high molecular weight (>100 000 AMU) decreased while that with low molecular weights (<1 000 AMU) increased. Ozonation increased the concentration of organic materials that totally resisted removal by carbon adsorption while both pH and DO had significant effects on some characterization parameters.

Klaning *et al.*[134] evaluated thermodynamic parameters for the reaction of chlorite ion with ozone. Klaning and Wolff[135] conducted experiments on the reactions of chlorine and bromine atoms. Tee *et al.*[136] examined the bromination of p-hydroxybenzoic acid in aqueous solution. Tee and Iyengar[137] also noted the bromination of phenol. Kasiyanchuk *et al.*[138] reported on the decomposition of aliphatic amines in dilute aqueous solutions as affected by chlorine and ozone.

Meier *et al.*[139] assessed chromosomal damage and sperm-head abnormalities in mice caused by common water disinfectants and related chemicals: chlorine, monochloramine, chlorine dioxide, sodium chlorite, and sodium chlorate. Oral administration of chlorine of pH 8.5 at dose levels equivalent to approximately 4 and 8 mg/Kg·d induced significant increases in the level of sperm-head abnormalities. There was no evidence of other effects with any of the disinfectants or with halogenated acetonitrites detected in mouse stomachs after oral dosing with sodium hypochlorite. Fulton[140] reviewed the techniques and chemicals used for drinking water treatment including disinfection. Ogita *et al.*[141] assessed the impact of hydrogen peroxide on the photo-induced decomposition of THMs.

Scully *et al.*[142] reported on the reaction of hypochlorite and organic N-chloramines in stomach fluids. Kopfler *et al.*[143] studied the reactions of chlorine in drinking water with humic acids and *in vivo*. Carlson *et al.*[144] characterized the products from the reaction of hydrobenzoic and hydroxycinnamic acids with aqueous chlorine, ClO_2 and chloramine. Wachter and Andelman[145] studied the nonpurgeable organohalide compounds resulting from the chlorination of algal extracellular material. Helz and Kieber[146] examined the impact of hydrogen peroxide in estuarine water on the water's chlorine demand.

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Optimization of treatment plant operation

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References which contain a large list of citations include last year's literature review,[1] and the proceedings of a joint U. S.-Japan Conference.[2] Reviews of treatment plant operation in various countries were reported on by a number of investigations.[3-8] These deal with a number of common operational problems such as odor, sludge bulking, nutrient removal and resource allocation.

MANAGEMENT, OPERATION, MAINTENANCE, AND TRAINING

A book on planning, design, and operation of treatment plants was prepared by Qasim.[9] A similar publication providing detailed standards and task statements for more than 600 individual tasks performed at treatment plants became available.[9] Publications aimed at improving the performance of treatment plants that are not meeting standards were provided by Stover and Cowan[10] and by the U. S. Environmental Protection Agency (EPA).[11] In both, improvement of operational procedures played the key role. The use of contract operation rather than in-house public service employees was addressed by several authors.[12,13] Other procedures for improving treatment plant performance include the use of effective management techniques,[14] record systems,[15] and video taping.[16] Video tapes were used to train personnel to install and maintain equipment properly.

PROCESS CONTROL AND MODELLING

Hartley[17] provided an overall presentation on the subject of activated sludge process control. He addressed operation and start-up procedures. Successful operation at low SRT was reported by Wilson *et al.*[18] Better effluent quality was achieved when SRT was less than 1 day. Mulbarger *et al.*[19] reported on the link between secondary clarifier performance and activated sludge treatment efficiency. The use of batch sedimentation tests and solids flux theory for design and operation was reported by Daigger and Roper.[20] Keinath,[21] Severin and Poduska,[22] and Chapman[23] also addressed techniques for controlling final clarifier performance. Activated sludge air diffuser performance was addressed by Sekizawa *et al.*[24] and by EPA.[25] Development of standard procedures for design, testing, operation, and control of fine bubble aeration systems was reported on by Boyle.[26]

Performance of RBC units was reported on by several investigators.[27,28] Organic overloading and mechanical failure of equipment were major problems. Removals achieved were somewhat lower than those claimed by manufacturers' literature.

Problems with tertiary filters were addressed by Young.[29] Poor clearing of the filter medium was the primary cause of problems. The use of high-scour backwash was recommended. Sludge handling modifications were reported on by Carrio *et al.*[30] and Ross and Crawford.[31] The former reported success in sludge volume reduction in the range of 15 to 67%.

INSTRUMENTATION AND AUTOMATION

Handbooks addressing the instrumentation and automation of treatment plants were published by several authors.[32-35] In one,[35] some of the new, more sophisticated treatment technology was addressed. Residual chlorine measurement and control was reported on by Kulin[36] and Finger *et al.*[37] The latter dealt with the problem of achieving a zero residual in an on-line system. The successful use of respiration rate for control of bio-reactors was reviewed by Miller.[38]

MISCELLANEOUS

Reduction of energy use at treatment plants was reported on by several investigators.[39-41] The use of heat pumps to extract energy from the wastewater was explored, as were more conventional techniques. Willcocks[42] explored the integration of a treatment plant into a district heating system. Wastewater treatment plant odor problems were addressed by Wheeler[43] and Waltrip and Snyder.[44] Hydrogen sulfide was the major problem and chemical oxidation was recommended for remediation. The corrosive effect of this chemical on treatment plant appurtenances was reviewed by EPA.[45] Narain *et al.*[46] addressed bacterial mediated corrosion problems. Cold weather problems were reviewed and remedies were suggested by Reed and Niedringhaus,[47] and Szelc.[48] Special features of operation and maintenance at water reclamation plants were addressed

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